Probing the Nitrogen Deficiency in Gallium Nitride by [71]Ga Magic-Angle Spinning NMR Spectroscopy

Woo-Sik Jung,* **Chinho Park, and Seunghun Han**

School of Chemical Engineering and Technology, College of Engineering, Yeungnam University, Gyongsan 712-749, Korea
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One of Group III-V nitrides, gallium nitride (GaN) with a bandgap of 3.4 eV at room temperature and its alloys with other Group III-V nitrides, aluminum nitride (AlN) with a bandgap of 6.2 eV and indium nitride (InN) with a bandgap of 1.9 eV, are candidate materials for light emitting diodes having engineered bandgaps with energies from the visible to the deep UV region.[1] Sapphire is the most widely used substrate for the thin-film growth of GaN. However, there exists severe mismatch both in lattice parameters and thermal expansion coefficients. Such a large mismatch induces stresses in the first few layers of GaN grown on sapphire. A trend for the future is, therefore, the development of GaN substrates for homoepitaxy by fabricating GaN bulk single crystals and wafers. Sublimation[2] and high-pressure solution methods[3] are considered for crystal growth of GaN. The methods demand the availability of well-characterized GaN powder source with high purity and single phase. Up to now most investigators have employed the powder X-ray diffraction (XRD) to determine whether or not GaN powder synthesized is of high purity and single phase.[4] But nitrogen-deficiency in the GaN can be hardly revealed by the powder XRD, though GaN is apt to be nitrogen deficient in its synthetic process.

In this report we show that the nitrogen-deficiency in GaN can easily be probed by [71]Ga magic-angle spinning (MAS) NMR spectroscopy. The GaN powders were prepared by the solid-gas reaction of gallium oxide (β-Ga$_2$O$_3$) and α-gallium sulfide (α-Ga$_2$S$_3$) with ammonia at various temperatures, and then characterized by XRD and [71]Ga magic-angle spinning (MAS) NMR spectroscopy.

Experimental Section

The precursor materials, β-Ga$_2$O$_3$ (Wako Pure Chemical Industries, 99.99%) and α-Ga$_2$S$_3$ (Aldrich Chemical., 99.99 %) powders were used without further purification. The precursor powder in an alumina crucible was set in an alumina tube with an inner diameter of 36 mm and heated under a flow of ammonia (Showadenko Co., 99.999%) in the temperature range 800-1100 °C for 3h. The flow rate of ammonia was 50 mL min^{-1}. The sample was taken from the furnace after it was cooled to the room temperature under a

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*Corresponding author. Phone: +82-53-810-2528; Fax: +82-53-814-8790; E-mail: wsjung@yu.ac.kr

flow of ammonia. The process of conversion of β-Ga$_2$O$_3$ and α-Ga$_2$S$_3$ to GaN was investigated by XRD (Rigaku DMX-2500 diffractometer with Cu-Kα radiation operating at 40 kV and 100 mA) and [71]Ga magic-angle spinning (MAS) NMR spectroscopy. High-resolution [71]Ga MAS NMR spectra were recorded at ambient temperature using a Bruker DSX 400 spectrometer running at 122.0 MHz and a Varian Unity INOVA 600 spectrometer running at 180.3 MHz. The zirconia rotor used as sample chamber was spun at 14 kHz during data collection. Single-pulse excitation was employed with the exception of α-Ga$_2$S$_3$ where Hahn echo excitation sequences ($\pi/2$-τ-π-acquisition) were employed. Chemical shifts (δ) were referenced to 1 M aqueous gallium nitrate solution. Room-temperature photoluminescence (PL) measurements were carried out by using a He-Cd laser ($\lambda = 325$ nm).

Results and Discussion

The precursor material, α-Ga$_2$S$_3$ powder was nitridated at different reaction temperatures for 3 h. Each powder obtained was characterized by XRD and [71]Ga MAS NMR spectroscopy. Figure 1 shows XRD patterns of samples synthesized at different temperatures. In the sample nitridated at 800 °C weak diffraction peaks assigned to GaN[5] were detected together with those assigned to α-Ga$_2$S$_3$.[6] The intensities of the former peaks increased and those of the latter peaks decreased with the reaction temperature. In the case of the sample nitridated at 1000 °C, there were no detectable peaks other than the peaks assigned to GaN, as shown in Figure 1(d). In a previous paper[7] we reported the results on the reaction of β-Ga$_2$O$_3$ with ammonia. The comparison of XRD patterns at various temperatures between α-Ga$_2$S$_3$ and β-Ga$_2$O$_3$[7] shows that the reactivity of α-Ga$_2$S$_3$ with ammonia is a little lower than that of β-Ga$_2$O$_3$. The low reactivity is ascribed to the high affinity of gallium for sulfur, thereby stabilizing Ga$_2$S$_3$ thermodynamically. It is noteworthy that the reactivity of Al$_2$S$_3$ with ammonia was much higher than that of Al$_2$O$_3$.[8]

Solid-state NMR spectroscopy might be a more powerful probe than XRD in characterizing less crystalline materials because the latter provides little information about central-metal distribution owing to lack of long-range order. The NMR spectroscopy is also a useful tool for identification of defects in crystal structure. Figure 2 shows [71]Ga MAS NMR spectra (acquired at 122.0 MHz) of samples synthesized at
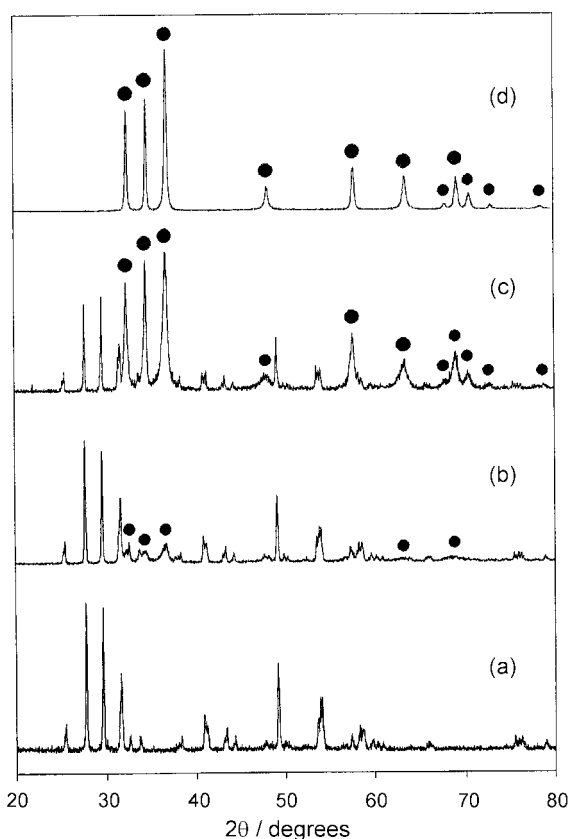
Figure 1. XRD patterns of α-Ga$_2$S$_3$ powder (a) before and after nitridation in flowing ammonia at various temperatures for 3 h: (b) 800 °C, (c) 900 °C, and (d) 1000 °C. The peaks marked with closed circle are assigned to GaN.

Figure 2. 122.0 MHz ^{71}Ga MAS NMR spectra of α-Ga$_2$S$_3$ powder (a) before and after nitridation in flowing ammonia at various temperatures (b, c, d) for 3 h.

Figure 3. Room-temperature PL spectra of the powders obtained by nitridation of (a) β-Ga$_2$O$_3$ and (b) α-Ga$_2$S$_3$ at 1000 °C for 3 h.

different temperatures. The poorly resolved spectrum of α-Ga$_2$S$_3$ was obtained by employing Hahn echo excitation sequences, indicating that the quadrupole coupling of Ga atom in α-Ga$_2$S$_3$ is very high. There are three polymorphs of Ga$_2$S$_3$. In the α-Ga$_2$S$_3$ the sulfide lattice is of the wurtzite ZnS type and the Ga atoms have an ordered arrangement. As shown in Figure 2(b) and (c), the peaks assigned to α-Ga$_2$S$_3$ were not observed by employing single-pulse excitation. In the case of the sample nitridated at 800 °C for 3 h, there were no detectable peaks other than the peak at 325 ppm assigned to GaN.[9] With increasing the reaction temperature the peak of GaN became more narrow because of increase in crystallinity. It is interesting that there was also a broad peak at 425 ppm for the samples nitridated at 1000 and 900 °C for 3 h, though their XRD patterns show that they were GaN and a mixture of α-Ga$_2$S$_3$ and GaN, respectively. The chemical shift of the broad peak was temperature independent within experimental error. The broad peak had not been observed in the conversion of β-Ga$_2$O$_3$ to GaN under a flow of ammonia below 1000 °C,[7] but was observed for samples nitridated at 1050 and 1100 °C for 3 h. Such a broad peak was observed for commercially available GaN powders,[9] but the peak has not been characterized yet in detail.

The broad peak at 425 ppm is not due to Ga metal because the chemical shift of paramagnetic Ga metal is temperature dependent,[10] but is due to the nitrogen-deficient GaN
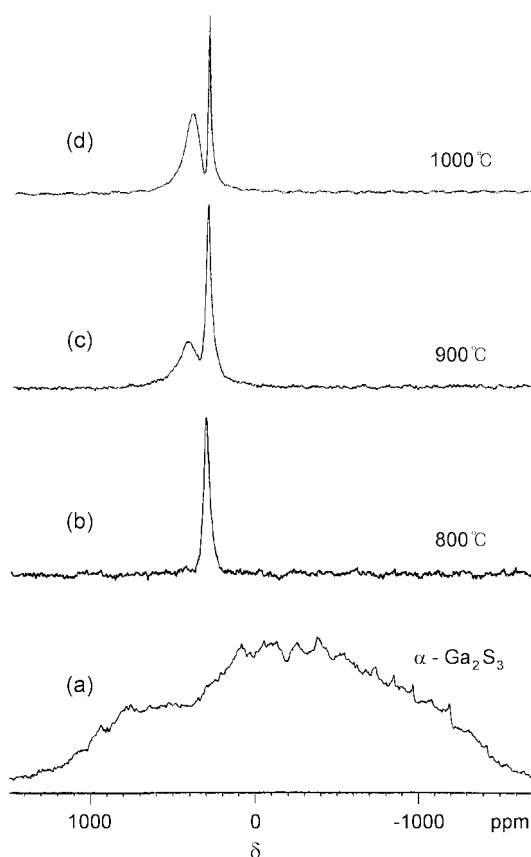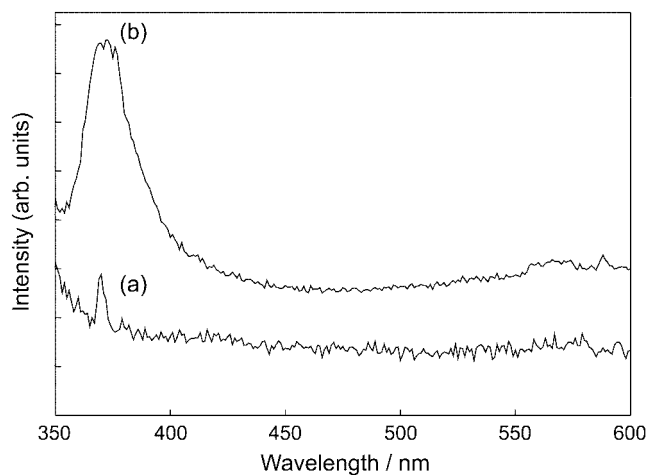
(GaN$_{1-x}$ where $0 < x < 1$). Considering that within a given family of Ga compounds, the chemical shift moves generally to high frequency as the number of coordinated ligands decrease,[11] it may be reasonable that the resonance of GaN was *ca.* 100 ppm high-frequency shifted by the nitrogen deficiency (*i.e.*, by decrease from four to three or less in coordination number of Ga).

The PL spectrum of the nitrogen-deficient GaN powder

(which was obtained by nitridation of α-Ga$_2$S$_3$ at 1000 $^{\circ}$C for 3 h) was compared with that of highly pure and single-phase GaN powder (which was obtained by nitridation of β-Ga$_2$O$_3$ at 1000 $^{\circ}$C for 3 h). As shown in Figure 3, the emission peak for the latter (Figure 3(b)) was much broader than that at 370 nm for the former (Figure 3 (a)).

Although GaN decomposition has been extensively studied, there are substantial differences in the reported kinetic parameters and decomposition mechanisms. The nitrogen deficiency in GaN was usually found for samples prepared at high reaction temperatures above 1000 $^{\circ}$C. But long duration time also caused the deficiency even at relatively low reaction temperatures. For example, the XRD pattern of the sample obtained by nitridation of α-Ga$_2$S$_3$ at 800 $^{\circ}$C at 170 h showed that it was almost GaN mixed with a very small amount of unreacted α-Ga$_2$S$_3$, but its 180.3 MHz ^{71}Ga MAS NMR spectrum exhibited a broad and intense peak at 404 ppm besides the peak assigned to GaN.

In summary, this work shows that GaN powder synthesized should be characterized by the powder XRD as well as ^{71}Ga MAS NMR spectroscopy. The latter is the powerful tool for identification of the nitrogen-deficiency in crystalline GaN, which can be not easily revealed by other instrumental methods such as XRD.

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